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Research Article

Sulphur and Nitrogen Fertilization as a Potential Means of Agronomic Biofortification to Improve the Content and Uptake of Microelements in Spring Wheat Grain DM

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The aim of the field experiment was to analyze the impact of various nitrogen and sulphur doses on the content and uptake of spring grains of iron, manganese, copper, and zinc. The study was conducted in southeastern Poland (2009–2011) on Cambisols (WRB 2007), in conditions of low soil sulphur content. The experiment included 4 doses of N fertilization (0, 40, 80, and 120 kg/ha) and 2 doses of S application (0 and 50 kg/ha). The analysis showed that fertilization with nitrogen and sulphur had a positive effect on the studied features of spring wheat. The combination resulted in beneficial content of Fe, Mn, Zn, and Cu (Fe 45.00, Mn 35.67, Zn 34.63, and Cu 3.65 mg/kg) and beneficial uptake of microelements by grain DM (Fe 216.1, Mn 171.3, Zn 166.4, and Cu 17.52 g/ha). The highest grain yield (5.43 t/ha) was obtained after the application of nitrogen at a dose of 80 kg/ha and sulphur at a dose of 50 kg/ha. In relation to control, this increase of grain yield amounted to 13.3%. Significant correlations were also found between grain yield and the content and uptake of all microelements, as well as between elements. No significant correlation was found only between the content and uptake of Fe and the content of Mn and between the content of Mn and Cu. Sulphur supplementation of NPK fertilization can be a good means of agronomic biofortification for spring wheat in order to increase the content and uptake of micronutrients such as Fe, Mn, Zn, and Cu.

1. Introduction

At the present time, cereals became the basis of human nutrition and possible source to maintain and improve health. According to the food pyramid proposed by the National Food and Nutrition Institute, low-processed products of grain and seeds from cereal are at the base of the pyramid and should be consumed as the most important source of nutrients in the human diet. In Poland, cereal products meet about 50% of the daily requirement for these minerals, especially P, K, Mg, Fe, Zn, and Cu [1].

An important agricultural problem in many countries in Europe and all over the world is the deficiency of sulphur in arable soils due to a major tightening of environmental regulations at the end of the twentieth century [2–5]. In Polish soils in 2015, low content (I) of sulphate sulphur was found in 198 monitoring points (91.7% of all profiles), which was a similar result to that observed in 2010. Medium natural content (II) was shown for 10 profiles and high natural content (III) for 6 profiles. The level of sulphate sulphur was within the range referred to as anthropogenically elevated (IV) only in two samples. There has also been a perceptible drop in the mean sulphur content over the years, from 1.38 to 1.00 mg $S\text{-}SO_4$/100 g, respectively, in 1995 and 2015 [6]. This phenomenon may cause a deficit for sensitive crops. In addition, it may affect the disturbance in effectiveness of NPK applied in the fertilizers, especially in nitrogen metabolism [4].

Nitrogen and sulphur are very important protein components; thus, the correct N : S ratio results in improved crop yields and quality. Many interactions occur between sulphur and nitrogen in the plant at various levels, such as uptake, assimilation of NO_3 and SO_4^{2-}, and formation of metabolites of N and S [4]. In the case of low content of absorbed sulphur, "minimum law" may occur, which means that high nitrogen fertilization will affect the low use of sulphur by plants. As a consequence, the content of sulphur and its compounds in plants is reduced. Both thesenutrients are necessary in human and animal diets [4].

People need at least 22 mineral elements for their wellbeing. Crop plants are an important source of food in the human diet and are also used as animal feed in fresh or processed forms. Therefore, their nutritional values and the proportion of nutrients they contain are very important for human and animal health [7]. However, it has been estimated that a considerable proportion of people worldwide suffer from deficiencies of mineral components such as iron, zinc, iodine, cooper, selenium, calcium, and magnesium.

Malnutrition in microelements is called "hidden hunger." This problem affects more than half of the human population in the world. Especially women and children in many developing countries suffer from a deficiency of micronutrients. The deficiency of iron, vitamin A, zinc, and iodine has been the main cause of diseases in the world since the twentieth century [8–10]. The main reason for the hidden hunger is the reduced intake of vegetables, fruits, meat, and fish, which are rich in minerals [11]. The provision of micronutrients to the diet affects the normal course of metabolic functions in the human body [12].

Conventional methods of mineral elements supplementation are related mainly to direct supplementation with elements, varied diet, and enrichment of food [13]. A helpful way of supplementing the shortage of elements in plants, especially in the edible parts (grains and tubers) may be biofortification [14–16]. Agronomic or genetic methods can be used for this purpose [17].

1.1. Biofortifiaction. The idea of biofortification into micro and macroelements is interesting in order to improve the growing conditions of plants and improve the yield and quality of arable crops. In addition to mineral fertilization, conventional breeding, and transgenic plants, intercropping between docots and gramineous species could be the key to biofortification of some staple crops [18]. Table 1 presents the methods used to increase the intake of microelements.

1.2. Strategies in Agriculture for Increase of Micronutrient Concentrations in Plant Foods. In modern agriculture, it is important to know the effects of fertilizers and fertilization techniques. Through this knowledge, we can influence the change in the content of macro- and microelements in plants and improve plant quality [19]. Especially in countries where cultivation of cereals is based on modern varieties and proper fertilization can influence the increase of yield and the contents of iron and zinc in them [20, 21]. For example, experiments conducted in Turkey showed that the use of zinc for wheat fertilization had an impact on the increase in yield by 500% [21].

The addition of micronutrients for fertilization may improve the yield and quality of wheat grain, but appropriate fertilization methods should be applied. For example, on limestone soils, beneficial effects are obtained by zinc supplementation in the early period of grain pouring [22]. The content of several microelements can be increased at the same time by using appropriate multicomponent fertilizers, for example, fertilizers containing zinc, selenium, iodine, copper, and nickel [23, 24]. The manganese content can be increased at a later stage of cereal development by applying liquid fertilizers as spray on the plants [25]. Many studies have shown the possibility to increase the content of N, P, K, Na, Ca, Mg, Zn, Mn, Cu, Fe, and Se in potato edible parts and cereal grains by using sulphur fertilizers [26–28]. Supplementation of NPK fertilizers with sulphur enforces sulphur deficiency in soils [29, 30]. Of particular interest is the use of elemental sulphur, which reduces losses when the threat of sulphate sulphur leaching to the ground water occurs. Also, through the slow decomposition of elemental sulphur, its long-lasting effect is seen. In addition, the oxidation of elemental sulphur decreases the soil pH, especially in alkaline soils, and thus increases the availability of micronutrients to plants [29, 31]. In addition, the use of organic fertilizers, especially manure, increases the content of many microelements in soils and then their availability to plants [19].

Table 1: The methods used to increase the intake of micronutrients [18].

Method	Description
Fortification	Addition of micronutrients to food during processing
Supplementation	Consumption of micronutrient supplements, e.g., in the form of tablets
Biofortification	Increased content of micronutrients in basic food products
Agronomic biofortification	The use of micronutrient fertilizers

Crop rotation is the basic way to improve the yield and quality of the succeeding plant. The leguminous plants show a particularly favorable effect on the yield, quality, and weed infestation of cereals. The improved nitrogen balance is also important in this case [19]. One of the recommended measures is multiple cropping (polyculture), which increases species diversity in fields as well as the stability of agrosystems. The general category of intercropping includes four subcategories: mixed intercropping, row intercropping, relay intercropping, and strip intercropping [32]. The most common form of multiple cropping is mixed cropping of cereals, and cereals with legumes. In this system, individual species can exploit different resources or the same resources more efficiently, which can increase total yield per unit area in comparison with the cultivation of a single species [33–35].

Tillage systems is a very important factor in plant production. The long-term use of minimum tillage or direct sowing is especially known in the negative sense. These soil tillage methods tend to increase the soil density and poor distribution of nitrogen, phosphorus, and micronutrients in the soil profile. This, in consequence, affects the inadequate uptake of ingredients and may cause a change in the yield and quality of plants [19, 36–38].

In the past, *plant breeding* was used more to obtain higher yields of arable crops, where no attention was paid to the quality of the crop [39, 40]. For example, the yield of wheat grain has more than tripled in relation to the yield achieved in the early twentieth century to the amount of 860 kg/ha [41, 42]. However, as it turns out, the higher yielding cereals contain smaller amounts of elements in the grain [43, 44]. In order to improve this condition, it is proposed that the old varieties from the gene bank should be crossed with modern high-yielding varieties [18, 45].

Genetic engineering aims to change the characteristics of plants by adding foreign DNA to it or by modifying existing DNA in plants [19]. Currently, there are many studies in the world concerning the enrichment of plants with iron, zinc, and provitamin A. An example of this is the international HarvestPlus program implemented by many research institutes centered in CGIAR [46]. It aims to produce foods rich in Fe, Zn, and vitamin A in poor countries where they are deficient.

1.3. Micronutrient Status in Soils and Plants. Biofortification can be defined as an increase of the mineral status of agricultural plants by applying soil fertilization or foliar fertilization of plants and, as a consequence, improving their quality [22].

As research shows, the content of micronutrients in plants depends on their content in soil and on other factors that affect their availability [47, 48]. The content of some micronutrients, such as Zn, Mn, and Fe, in plants is closely correlated to the content of these elements in the soil and with the pH of the soil. As stated, the content of Zn and Mn in the plant decreases with increasing pH. However, the content of copper in plant tissues depends on the share in soils of copper and organic carbon [11, 49]. Vicente et al. [50] noted that the availability of copper and other micronutrients for plants decreases when the soil pH is basic (pH above 7.0). At conditions of alkaline reaction, copper is strongly adsorbed by aluminum, iron oxides, and organic matter.

It is commonly claimed that the iron content in the soil is more changed by various factors than the iron content in the plant. For example, an increase in soil pH causes a decrease in iron content in the soil and its availability to plants. It was also shown that redox reactions affect the iron and manganese content, which depend, among other things, on the degree of soil moisture [47, 48].

Many studies indicate the existence of a positive correlation between the content of micronutrients in the plant. These correlations depend on various soil factors, for example, pH of the soil. This type of correlation occurs between Mn and Zn [47, 48]. Other factors that influence the correlation of Mn-Zn in the plant are the texture and content of organic carbon [47, 48]. Nube and Voortman [48] report the chemical similarity among zinc, iron, and magnesium, where these elements can compete for uptake by plants. Also, the high content of phosphorus in the soil can have a significant effect on reducing the availability of zinc for plants.

As shown by studies, plants with slow vegetation and low yield contain more microelements in the dry matter than plants with long vegetation and high yield [20, 21]. This phenomenon is called concentration and dilution of elements. It can be explained by the fact that when a plant produces high yields, it is not able to take from the soil an appropriate amount of chemical elements in accordance with the size of the biomass produced. Therefore, the elements taken in a small amount are diluted into a large biomass.

Due to a shortage of available sulphur in many regions of the world, it is necessary to use sulphur fertilization. It is of huge importance for the increase in yield of crop plants and improvement of their quality [29, 30, 51]. A very popular form of sulphur in agricultural crops is elemental sulphur. Its addition to the soil reduces the loss of sulphate sulphur by leaching, and its long period of decomposition favorably affects the entire crop rotation [3, 26, 27, 29]. Because elemental sulphur reduces the pH of the alkaline soil, it can improve the availability of phosphorus and micronutrients and reduce the occurrence of iron chlorosis [29, 51].

Research shows that zinc fertilization in the form of $ZnSO_4$ is a beneficial way of increasing grain yield and zinc content [52]. In the situation of low iron content in the soil, foliar fertilization with $FeSO_4$ can be applied. In the case of enrichment of plants with zinc, attention should be paid to nitrogen, which plays an important role in zinc uptake, especially during the grain pouring phase [21, 53–55]. Moreover, it was observed that after the use of appropriately high doses of nitrogen in the presence of foliar fertilization with micronutrients, both the share of zinc and the other elements increased [54, 56, 57].

1.3.1. Cereal Grains: An Important Source of Microelements. Grains of cereals such as rice, wheat, barley, maize, or sorghum are the most important element of the human and animal diet in the world [23, 58]. It is known that wheat is a symbol of the Mediterranean diet [59]. The global use of cereals in the world in the season 2016/17 constituted 2007 million tones, of which wheat alone amounted to 732 million tones [60]. The forecast predicts that, in the season 2017/2018, the general food demand for cereals will increase by 1.3% and the consumption per capita will amount to 148 kg/year, including wheat which amounts to 66.7 kg/year. As we know, cereals are the main source of micronutrients in human nutrition [56, 61].

In many regions, especially where there are shortages of micronutrients, wheat accounts for about 50% of the human diet. It is also a good source of macro- and microelements [59]. Based on the study by Lončarić et al. [62], it can be concluded that some Croatian wheat genotypes are characterized by a higher concentration of iron, zinc, and copper in the grains. Table 2 includes, *inter alia*, the results of these tests [63, 64].

1.4. Status of Sulphur. The regulations and laws regarding the reduction of sulphur dioxide emissions in Europe caused a shortage of available sulphur in the soil, which affected the balance of nutrients needed for arable crops [65–67]. Sulphur is a very important nutrient for plants and is taken in an amount similar to phosphorus. It is involved in many metabolic processes in plants and protects them from abiotic and biotic stresses (xenobiotics, pests, and diseases) [68, 69].

Table 2: Contents of microelements in grains of wheat (*Triticum aestivum* L.) (according to Teklić et al. [64]).

Fe (mg/kg)	Mn (mg/kg)	Zn (mg/kg)	Cu (mg/kg)
51.4 ÷ 60.5	34.9 ÷ 49.8	10.1 ÷ 17.1	4.7 ÷ 9.0
40.1	42.8	19.2	6.84
32.6 ÷ 46.6	15.1 ÷ 27.6	26.5 ÷ 36.5	0.7 ÷ 4.1
33.3	23.3	36.2	4.5
19.3 ÷ 29.8	25.9 ÷ 45.2	21.7 ÷ 47.1	3.2 ÷ 4.9
34.0 ÷ 41.0	24.0 ÷ 28.0	35.0	3.5 ÷ 4.4
21.6 ÷ 33.8	19.7 ÷ 36.8	21.2 ÷ 34.8	5.2 ÷ 8.1

Glutathione metabolism is especially important for plants [70, 71]. Another example is the mechanism of producing volatile sulphur compounds by Brassica in the case of a pathogen attack or the production of phytochelatins, which form complexes with heavy metals and detoxify them [65].

Cereals are generally not considered to be highly sensitive to sulphur deficiency in the soil. There are, however, studies refuting this hypothesis. A study by Klikocka and Cybulska [4] found that wheat responded significantly to sulphur deficiency in the early stages of development. The authors observed inhibition of the plant's growth due to a lack of sulphur and the presence of symptoms of malnutrition, i.e., yellowing of young leaves. This demonstrated that this element is essential for the functioning of wheat despite the low nutritional requirement of cereals for sulphur, which amounts to 15–20 kg·S/ha [30]. Visual symptoms of S deficiency can be detected as macroscopic changes in a single plant. Sulphur deficiency develops first on light soils. From a bird's eye view, these areas appear as irregularly shaped plots with a lighter green colour ("washouts"). Indicators of sulphur status in a plant can be divided into biological, chemical, and constituent parameters [65, 72]. *Biological parameters* are the amount of sulphate sulphur and glutathione in the tissues. *Chemical parameters* describe the S status of the plant as HI (hydroiodic acid) reducible S, acid-soluble S, and total S. *Composed parameters* concern the ratio of N : S and the fraction of sulphate sulphur in the total S content. The idea to use the N : S ratio is due to the fact that nitrogen and sulphur are the main elements in the synthesis of amino acids (Figure 1).

Appropriately chosen application rates for sulphur fertilization are particularly important in the case of intensive nitrogen fertilization. In this case, sulphur increases the utilization of nitrogen [4]. In S-deficient soil, the application rate should be 1/5 of nitrogen in the case of cereals, 2/5 for rapeseed, and 1/3 for beet [73, 74]. The decision to use sulphur fertilizers should be preceded by ascertainment of the current content of sulphur in the soil. In the case of cereals, sulphur fertilization is recommended at the beginning of the tilling stage [74]. In a study where two nitrogen application rates (90 and 120 kg·N/ha) were used, with supply of 36 and 27 kg·S/ha into the soil, grain yield increased by 0.7 and 0.4 t/ha in comparison with the control without N [73]. Slow-acting fertilizers containing sulphur (calcium sulphate, gypsum sulphate, elemental sulphur, or natural fertilizers) are applied no later than during postharvest cultivation following a previous crop. It is significant that the effect of fertilization extends several seasons, and utilization of S amounts to about 35% [75]. Moreover, sulphur can be applied to the plant leaves (foliar application) using magnesium sulphates. Sulphur can be applied at a doubled or tripled rate. It can be applied in autumn in slow-acting and mixed fertilizers. The fertilizer requirement of spring wheat for sulphur is reduced by about 25% due to lower yield [76].

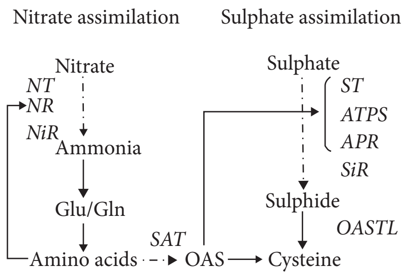

Figure 1: Scheme of assimilation of nitrates and sulphates and a combination of these processes by *O*-acetylserine (OAS) [72, 73]. NT, nitrate transporter; NR, nitrate reductase; NiR, nitrite reductase; Glu/Gln, glutamic acid, glutamine; ST, sulphate transporter; ATPS, ATP sulphurylase; APR, APS reductase; SiR, sulphite reductase; OASTIL, *O*-acetylserine(thiol)lyase; SAT, serine acetyltransferase; OAS, *O*-acetylserine.

As fo now, however, no further publication is available about the impact of the N fertilization with additional S supplementation on the status of micronutrients (Fe, Mn, Zn, and Cu) in grains of spring wheat. The importance as well as the role of sulphur and nitrogen applied as the fertilization of spring wheat—grown on Cambisols (WRB 2007) with slightly acidic pH, classified as a good rye complex—was the subject of the empirical research presented in this paper.

2. Materials and Methods

The presented research comes from a three-year field experiment, located in south-eastern Poland (50°42′ N, 23°15′ E). A two-factor experiment was performed in a randomized split-plot design (in four replications). The soil in the experiment was defined as Cambisols (WRB 2007) (sand 68%, silt 31%, and clay 1%). On the basis of chemical analysis of the soil, a high content of phosphorus, an average content of K and Mg, and low total and available sulphur were found. The soil reaction was slightly acidic (Table 3). Data on meteorological conditions are described in Table 4. On the basis of rainfall and air temperature during the vegetation period (March-August), the Selyaninov's hydrothermal coefficient was calculated (Table 4). According to the calculations, the 2009 growing season was defined as rather dry, borderline to the optimal one (1.3), while the other two vegetation seasons (2010, 2011) were determined as optimal to rather wet (1.6).

The subject of the presented research is a qualitative variety, Tybalt, of spring wheat (*Triticum aestivum* L.) (group A). Wheat was fertilized with various doses of nitrogen and sulphur, as shown in Table 5. 34% ammonium nitrate was used as a nitrogen fertilizer. Sulphur was used in

Table 3: Chemical characteristics of the soil (before sowing).

Specification	Method of analysis	Unit of measure	Year 1 (2009)	2 (2010)	3 (2011)
pH (0.01 mol/L $CaCl_2$)	Potentiometry with a methrohm-605 pH-meter	—	5.6	5.7	5.8
C-total	Combustion by LECO EC-12®	g/kg	9.2	8.9	7.7
N-total	By Kjeldahl's method		0.9	0.9	0.7
N min	$N\text{-}NO_3$ + $N\text{-}NH_4 \times 1.38$ (soil bulk density, mg/m^3) (PN-R-04038:1997)	kg/ha	72.8	68.4	64.9
P-available	Double lactate extraction and measurement by colorimetric assay by using the Egner Riehm DL method (PN-R-04023:1996)	mg/kg	54.5	53.5	48.3
K-available	Extraction: see above phosphorus and measurement by the photometric method (PN-R-04022:1996)		88.6	85.2	79.6
Mg-available	Extraction by 0.0125 m/L $CaCl_2$ and measurement by AAS (PN-R-04020-1994)		34.8	33.7	35.1
S-total	By ICP-AES mineralization with HNO_3 + $Mg(NO_3)_2$		102.8	86.3	72.0
$S\text{-}SO_4$-available	Extraction with 0.025 m/L KCl and measurement by ion chromatography		14.2	12.6	10.3

Table 4: Selyaninov's hydrothermal coefficient, sum of precipitation (mm), and mean air temperature (°C) in growing seasons (2009–2011), and the long-term averages from 1971 to 2005 (meteorological station in Zamość).

Years	Months (k)						Sum – mean (III-VIII)		
	III	IV	V	VI	VII	VIII	k^*	p	t
2009	5.3	0.5	2.4	2.1	0.4	0.8	1.3	349.1	2652
2010	1.8	1.1	2.0	1.1	2.1	1.3	1.6	443.4	2715
2011	1.2	1.1	0.7	1.0	2.7	2.3	1.6	414.6	2581
1981–2005	5.1	1.8	1.5	1.6	1.7	1.0	1.6	367.7	2353

$^*k$, Selyaninov's hydrothermal coefficient ($k = (p \times 10)\sum t$); p, precipitation (mm); t, temperature (°C).

Table 5: The doses and phases of application of nitrogen (N) and sulphur (S) fertilizers.

Fertilizer	Dose (kg/ha)	Time of fertilization		
		Spring, before sowing	BBCH 30–31	BBCH 55–59
Nitrogen (N)	0	—	—	—
	40	40	—	—
	80	40	40	—
	120	40	40	40
Sulphur (S)	50	40	—	10

two forms, prior to wheat sowing as kieserite ($MgSO_4 \times H_2O$: 5.1% Mg and 20.0% S) and as a foliar application on the wheat during vegetation (BBCH 55–59) as Epsom salts (magnesium sulphate heptahydrate – $MgSO_4$ x $7H_2O$: 10.2% Mg and 32% SO_3). In the spring, prior to sowing the seeds, fertilization with phosphorus (in the form of 17.4% granulated triple superphosphate at a dose of 39.6 kg·P/ha) and potassium (in the form of 49.8% potassium salt at a dose of 83 kg·K/ha) was performed. The size of the experimental plots was 30 m^2 (5 m × 6 m).

Sowing of spring wheat was carried out between the third decade of March and the first decade of April, depending on the year. Grains of wheat were sown with a density of 500 plants per m^2. In Table 6, the chemicals used in the protection of spring wheat against pests are presented.

Grain yield (at 11% moisture content) was marked at BBCH stage 89-92, after the harvest from each plot. The analysis of the microelement of the samples was determined by atomic absorption spectrometry (AAS) using a Varian SpectrAA 280 FS spectrophotometer (Varian, Inc., Palo Alto, USA) (PN-EN-14084:2004). For microelement analysis, Varian lamp, current 5 mA, flame acetylene/air (stochiometric ratio) was used. The following wavelengths were used for the determination of iron (Fe), manganese (Mn), zinc (Zn), and copper (Cu): 248.3 nm, slit 0.2 nm; 279.5 nm, slit 0.2 nm; 213.9 nm, slit 1.0 nm; and 324.8 nm, slit 0.5 nm, respectively.

To perform statistical analysis of the obtained results, analysis of variance (ANOVA) was used with the Snedecor F test. The significance of differences was calculated using the Tukey test ($p = 0.05$). A comparison of the mean results with post hoc analysis was then made. The calculations were carried out using statistical program Statistica 10 (StatSoft Poland) and Excel 7.0.

3. Results and Discussion

Analysis of the presented results proved a significant positive impact of N application on the wheat grain yield and on content and uptake of nutrients: Fe, Mn, Zn, and Cu in spring wheat grain DM. Fertilization with S also had a positive effect on the characteristics tested, except for Mn. The addition of S to nitrogen fertilization significantly decreased Mn content in the grain, and a trend of reduced Mn uptake by grain DM was observed. Statistical analysis did not show any interaction between the experimental factors used, i.e., the dose of nitrogen and sulphur. However, it could be noted that the addition of sulphur to each nitrogen dose increases the yield of wheat grain and the content and uptake of the analyzed micronutrients, i.e., iron, manganese, zinc, and copper. The obtained result shows the so-called sulphur additive effect. Also, it was noticed that after adding sulphur to each dose of nitrogen, the yield and the content of micronutrients increases, although in the case of higher nitrogen doses these are already smaller increments. This

Table 6: Chemicals used in the protection of spring wheat against pests.

Pests	The pesticide	Active substance	Dose	BBCH stage
Weeds	Granstar 75 WG	Tribenuron-methyl	20 g/ha	BBCH 28
	Puma super 069	Fenoxaprop-P-ethyl	1 L/ha	
Fungi	Alert 375 SC	Flusilazole + carbendazim	1 L/ha	BBCH 30–32
	Tilt CB 39.5	Propiconazole + carbendazim	1 L/ha	BBCH 58–59
Insects	Decis 2.5	Deltamethrin	0.25 L/ha	

phenomenon is widely described in the literature and is known as the law of decreasing increments, or as the law of Mitscherlich [77]. Generally, it can be concluded that the additive effect of the elements proceeds when there is a constant increase in the characteristics (yield and nutrient content) as a result of supplementation of the second factor.

Based on the analysis of the available literature, we can conclude that the rate of uptake of minerals (macro- and micronutrients) depends on the crop species [78], variety [79], habitat conditions [80, 81], and other agronomic factors. The grain of wheat cultivated according to a medium-intensive technology contains (in mg/kg) 22.0 Fe, 21.6 Zn, and 2.55 Cu [78]. Another study found the following contents of these elements in wheat grain: 40.7–54.5 mg/kg Fe, 24.6–29.0 mg/kg Mn, 19.1–25.6 mg/kg Zn, and 1.81–2.20 mg/kg Cu [82].

3.1. Nitrogen. Based on the analysis of the research results from the presented experience, it can be stated that the highest grain yield of spring wheat was obtained after fertilization with 80 kg/ha of N (5.40 t/ha). Grain yield increased by 13.1% compared to the control. The use of nitrogen at a dose of 120 kg/ha N did not cause a significant increase in grain yield in relation to the previous dose. The concentration of micronutrients in the grain of spring wheat increased at the same time as increasing dose of nitrogen and was the highest after the use of 120 kg/ha N (Fe 45.37, Mn 37.48, Zn 35.00, and Cu 3.77 mg/kg DM) (see Table 7 and Table S1 in the Supplementary Material for comprehensive dataset analysis). The uptake of Fe, Mn, Zn, and Cu by grain DM also significantly increased at the same time as the increasing N application rate and was the highest after fertilization with 120 kg/ha N (Fe 224.7, Mn 185.4, Zn 173.5, and Cu 18.69 mg/ha) (see Table 6 and Table S1 in the Supplementary Material for comprehensive dataset analysis).

The literature provides much attention to nitrogen fertilization on grain yield, and quality and content of nutrients in wheat grain [83]. The analyzed literature describes the results of a field experiment in which the effect of three increasing doses of nitrogen on the content of micronutrients in wheat grain was investigated. It was found that the use of higher doses of nitrogen influences the increase in concentration of Fe, Zn, and Cu in grains but has no effect on the content of Mn [56]. Based on these observations, we can say that proper nitrogen fertilization is conducive to an increase in the concentration of nutrients in wheat grain, which is the basis of human food [56].

Based on research by Kutman et al. [84], we found that the use of high doses of nitrogen has a beneficial effect on the consumption of iron and zinc through wheat grain. In the studies of Xue et al. [54], the beneficial effects of nitrogen fertilization on the content and uptake of zinc by wheat have been demonstrated. This phenomenon was confirmed in subsequent studies by Kutman et al. [55], on the basis of which they write that a high dose of nitrogen favorably promotes the increase of Zn content in the grain and further improves phase of wheat tilling and grain development. As can be seen in the literature, the applied forms of nitrogen fertilizer have different effects on the content of manganese in the plant. Therefore, they can be arranged according to the tests in the following order: $(NH_4)_2SO_4 > NH_4NO_3 > Ca(NO_3)_2$ [82].

3.2. Sulphur. As shown in the presented studies, the addition of sulphur improves the NPK effect, and wheat grains increased by 3.6% (Table 7 and Table S1 in the Supplementary Material for comprehensive dataset analysis). According to Podleśna [73], the addition of 60 kg/ha of S caused an increase in winter wheat grain yield by almost 11%.

Our research showed that the concentration of Fe, Zn, and Cu in the wheat grain after sulphur application at a rate of 50 kg/ha increased about 6.5%, 4.8%, and 5.3%, respectively, in comparison with the control. However, the content of Mn was reduced by 5.4%. The uptake of Fe, Zn, and Cu by grain DM following application of 50 kg/ha S increased by 10.2%, 7.2%, and 8.8%, respectively, in comparison with the control.

The addition of S to NPK fertilization showed a tendency to decrease the uptake of Mn by grain DM (see Table 7 and Table S1 in the Supplementary Material for comprehensive dataset analysis). As can be seen from the studies of other authors, the iron-, zinc-, and copper-rich soil can successfully provide the amount of these elements appropriate for cereals. However, these microelements must be available for the plants [85]. Because sulphur reduces soil pH, it indirectly influences the availability of many microelements, including Zn, Fe, Mn, and Cu [86]. It has been observed that there may be a lot of iron in the soil, however, this element in the rhizosphere may be inaccessible to plants. Therefore, the addition of elemental sulphur to the soil may improve the availability of iron by changing (lowering) the pH [87].

3.2.1. Interactions and Correlation between Nutrients. In the presented studies, it was shown that the addition of sulphur to all doses of nitrogen did not significantly affect the content and uptake of the examined micronutrients, such as iron, manganese, zinc, and copper. However, the trend of content and uptake of nutrients was noticed, especially in

Table 7: The influence of nitrogen N and sulphur S fertilization on content (mg/kg) and uptake (g/ha) of microelements by spring wheat grain.

Fertilization		Grain yield (t/ha)	Fe		Mn		Zn		Cu	
S	N		Content	Uptake	Content	Uptake	Content	Uptake	Content	Uptake
0S (N ×SS)	0	4.03 a	38.53 a	137.4 a	35.00 a	152.2 a	31.03 a	114.4 a	3.15 a	11.24 a
	40	5.15 a	40.70 a	149.3 a	36.27 a	133.3 a	32.10 a	118.4 a	3.33 a	12.23 a
	80	5.36 a	41.87 a	189.9 a	38.23 a	181.8 a	33.53 a	160.1 a	3.46 a	16.45 a
	120	5.47 a	43.80 a	211.8 a	38.87 a	188.1 a	34.13 a	165.2 a	3.70 a	17.89 a
50S (N ×0S)	0	4.13 a	41.03 a	149.7 a	33.33 a	121.8 a	32.87 a	115.9 a	3.34 a	12.17 a
	40	4.38 a	42.70 a	165.4 a	35.30 a	137.1 a	33.77 a	131.3 a	3.52 a	13.67 a
	80	5.43 a	45.00 a	216.1 a	35.67 a	171.3 a	34.63 a	166.4 a	3.65 a	17.52 a
	120	4.72 a	46.93 a	237.6 a	36.10 a	182.8 a	35.87 a	181.7 a	3.85 a	19. 50 a
Mean (S)	0S	4.75 B	41.23 B	174.4 B	37.09 A	157.1 A	32.70 B	138.8 B	3.41 B	14.45 B
	50S	4.92 A	43.92 A	192.2 A	35.10 B	153.2 A	34.28 A	148.8 A	3.59 A	15.72 A
Mean (N)	0N	4.08 B	39.78 D	143.6 D	34.17 C	123.5 D	31.95 D	113.6 D	3.24 D	11.71 D
	40N	4.27 AB	41.70 C	157.4 C	35.78 B	135.2 C	32.93 C	124.9 C	3.43 C	12.95 C
	80N	5.40 A	43.43 B	207.5 B	36.95 A	176.6 B	34.08 B	3.55 B	3.55 B	16.99 B
	120N	5.59 A	45.37 A	224.7 A	37.48 A	185.4 A	35.00 A	3.77 A	3.77 A	18.69 A
Mean (Y)	2009	4.74 B	45.11 A	191.1 A	34.46 C	145.5 B	32.93 B	139.3 B	3.62 A	15.34 B
	2010	4.68 B	40.74 B	169.7 B	35.84 B	148.6 B	30.20 C	125.6 C	3.34 B	13.88 C
	2011	5.09 A	41.86 B	189.1 A	37.99 A	171.5 A	37.35 A	166.6 A	3.54 A	16.03 A

Different letters in the same column indicate significant differences between results at $P \leq 0.05$.

combinations where nitrogen fertilization was applied at doses of 80 and 120 kg/ha, together with 50 kg/ha of sulphur. These results were arranged in accordance with the law of diminishing returns (Mitescherlich's law) [68]. Because the addition of sulphur to higher doses of nitrogen caused a smaller increase in the content and uptake of micronutrients.

In the world of plants and the plant itself, there is interaction (mutual positive or negative interaction) in the extraction of minerals from the soil. The addition of mineral fertilizers to the soil also affects the uptake of various nutrients, especially when the soil solution has excessive content of one component [88]. The interaction of chemical elements can take place on the surface of the roots or in the plant. Interactions can be divided into two main groups. The first group includes interactions that take place between ions. An example of this interaction is the liming treatment of acidic soils, which consequently reduces the content of micronutrients in the soil. However, the addition of lime to the soil does not change the content of molybdenum, and, for example, copper is more related to the organic substance than zinc and the increase in pH (as a result of liming) restricts the zinc uptake by plants more [89]. The second group of interactions is the relationship between ions, which have chemical similarity in their transport and their similar functions on the surface of the root or in the tissues of plants. Such ions have similar size, charge, and electronic configuration [90]. The interaction of anion-cation and anion-anion are usually competitive. However, often when using two minerals (for example in the form of mineral fertilization), there is a positive interaction (synergy), resulting in a higher yield and higher content and uptake of these chemical elements [91]. On the other hand, if the addition of two chemical elements reduces the plant yield compared to the addition of only one component, it is called negative (antagonistic) interaction. Where the addition of chemical elements does not cause changes, interaction does not occur.

In the presented experiment it was shown that the addition of sulphur to each applied dose of nitrogen caused a trend of increasing yield of spring wheat grain, and the content and micronutrient uptake. As was previously stated, this type of nitrogen and sulphur interaction affected the additive interaction of sulphur [91]. It is commonly known that the assimilation of nitrogen and sulphur in plants is closely related to each other (Figure 1) [89]. Therefore, joint fertilization with nitrogen and sulphur significantly influences the uptake and metabolism of these elements in the plant. The ratio of nitrogen to sulphur in proteins is regarded as a reliable indicator of sulphur supply in plants. According to Oenema and Postma [92], its proper value amounts to 15 : 1. In a study by Klikocka and Cybulska [4], the average N : S ratio in spring wheat was greater by about 21 : 1. Nitrogen fertilization increased the N : S ratio, while sulphur fertilization did not affect it. In the studies of Randall et al. [93], it was shown that as a result of using different doses of nitrogen and sulphur, the ratio of N : S in wheat grain protein ranged from 12 to 25.

Significant positive correlations were observed between the grain yield, and the concentration and uptake of all microelements in wheat grain DM. The correlation coefficients between grain yield and the content of micronutrients decreased in the order Cu > Fe > Zn > Mn. However, in the case of the correlation between grain yield and uptake of microelements by grain DM, the strength of the relationship was in the order Cu > Fe > Mn > Zn. Many authors report that more microelements in the dry matter accumulate in plants that have a long growing season and produce a low yield. On the contrary, when plants have a short growing season and high yields, small amounts of

Table 8: Correlation coefficients between grain yield and content and uptake of micronutrients.

Test feature (n = 24)	No.	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Yield of grain	(1)	**0.604**	**0.954**	**0.531**	**0.949**	**0.583**	**0.923**	**0.720**	**0.967**
Fe content	(2)	—	**0.812**	−0.095	**0.424**	**0.431**	**0.591**	**0.911**	**0.753**
Fe uptake	(3)	—	—	0.340	**0.844**	**0.577**	**0.893**	**0.863**	**0.987**
Mn content	(4)	—	—	—	**0.769**	**0.530**	**0.602**	0.225	**0.455**
Mn uptake	(5)	—	—	—	—	**0.639**	**0.923**	**0.632**	**0.899**
Zn content	(6)	—	—	—	—	—	**0.842**	**0.643**	**0.643**
Zn uptake	(7)	—	—	—	—	—	—	**0.773**	**0.936**
Cu content	(8)	—	—	—	—	—	—	—	**0.870**
Cu uptake	(9)	—	—	—	—	—	—	—	—

Bold letters represent significant differences ($P = 0.05 = 0.406$ and $P = 0.01 = 0.517$).

micronutrients are accumulate in the dry matter, regardless of their content in the soil [20, 21]. This is the concentration-dilution phenomenon, which was not, however, confirmed in the presented study.

On the basis of observations with the use of increasing doses of sulphur, Inal et al. [94] found that there is a positive correlation between the sulphur dose and the content of this element in the plant. However, the addition of sulphur to NPK fertilization does not affect the increase of sulphate sulphur in the soil.

In the presented experiment, a positive correlation between the tested micronutrients was found. There was only a significant correlation between the content and uptake of Fe and the Mn and additionally between the Mn content and the Cu content (Table 8). Based on the studied literature, it can be concluded that metallic elements can compete with iron and, as a consequence, limit iron uptake by the plant. It has been known for a long time that iron and manganese compete in the process of ion uptake by the plant [95]. Mn^{2+} ion is characterized by similar properties as alkaline cations (Ca^{2+} and Mg^{2+}) and heavy metals (Fe^{2+} and Zn^{2+}), therefore these ions compete with manganese for uptake and transport in the plant [96]. Negative correlation between iron and copper content in durum wheat was also observed, which may indicate mutual antagonism of elements and can be a reason of iron deficiency in the plant [97].

It is well known that a shortage of one element may increase the uptake of one or more of other chemical elements [98]. It has been shown that in the conditions of a nutrients shortage in the soil, there is a competition for their uptake, especially between Mn^{2+} and Cu^{2+} or Zn^{2+} [99] and between Fe^{2+} and Zn^{2+} or Cu^{2+} [100].

3.3. Weather Conditions. In the present study, the grain yield as well as content and uptake of microelements were modified by the weather. The sum and distribution of precipitation are known to play a major role in determining of yield. The yield was dependent on the number of days with precipitation from March to July. Grain yield was about 0.7 t/ha greater with 80 days of precipitation than in the case with 58 days of precipitation [101]. Dry periods in April are conducive to spring wheat yield, but they reduce its yield in May and June [102]. Spring wheat shows the greatest need for precipitation in June. The optimum precipitation during this period is about 100 mm, this factor has been shown to increase yield by 0.98 t/ha in conditions of good wheat in complex soil, and by 0.41 t/ha in very good rye complex [103]. The critical period of demand for water in cereals occurs from the stem elongation stage (BBCH 31) to the watery-ripe stage (BBCH 71) [91]. A shortage of water during this period reduces the number of grains per unit area, which usually means a decrease in yield, whereas 1,000 grain weight is formed following seed-setting and depends mainly on the availability of moisture (in addition to nitrogen and potassium) and on temperature (and sulphur supply) [77]. High temperatures cause intensive hydrolysis of leaf proteins, thus degrading chlorophyll, which contains nitrogen. As a consequence, the leaves accumulate less carbon dioxide, photosynthesis is reduced, and the grain-filling period is shortened, leading to lower 1,000 grain weight. This period is critical for sulphur as well [77].

The content and uptake of micronutrients by grain DM, except Fe content, were most favorable in the meteorological conditions in 2011 (rather wet). In the 2009 season (rather dry), the meteorological conditions also had an important effect on beneficial Cu content, and on Fe concentration and uptake by grain DM. In general, the content and uptake of microelements were the smallest in 2010 (rather wet) (Table 7). This may be due to the fact that there was very little precipitation during the grain formation and ripening stages (June and late July and August). As confirmed by Woźniak and Stępniewska [81], the described relationships showed the lowest content of cooper in the grain harvested in the year with a lower rainfall and higher air temperature, as in the present study. However, the concentration of Fe, Mn, and Zn in the wheat grain in the abovementioned study was not significantly affected by weather conditions, in contrast to the present results.

4. Conclusions and Recommendation

Based on the presented research and the literature, it can be said that sulphur fertilization should be applied on arable soils in the analyzed region. The experiment showed that presowing application of sulphur in the amount of 40 kg/ha in the form of granular kieserite and top dressing with magnesium sulphate hepatahydrate (10 kg S/ha) in combination with nitrogen fertilizer (ammonium nitrate) in the rate of 80 kg/ha is sufficient to achieve optimal grain yield

(5.43 t/ha); beneficial concentration of Fe, Mn, Zn, and Cu (Fe 45.00, Mn 35.67, Zn 34.63, and Cu 3.65 mg/kg); and beneficial uptake of microelements by grain DM (Fe 216.1, Mn 171.3, Zn 166.4, and Cu 15.52 g/ha).

As you know, modern agriculture in Europe and in Poland is conducted on the basis of an integrated system. Therefore, the dose of used mineral fertilization should be below their uptake. Therefore, when analyzing the results of this experiment, it is recommended to fertilize spring wheat using nitrogen in a dose of 80 kg N/ha with the addition of sulphur in the amount of 50 kg/ha. As it was shown in previous studies, this combination of fertilization in the dry mass of spring wheat (grain + straw) was 153.6 kg N/ha and sulphur 12.36 kg/ha) [4]. The proposed nitrogen fertilization rate and the high content of N_{min} availability in the soil (64.9 kg/ha) [4] will meet the demand of spring wheat for nitrogen. However, due to the low content of sulphur dioxide (SO_2) in the air and sulphate sulphur ($S\text{-}SO_4$) in the soil, greater amounts of sulphur fertilizer must be applied. Therefore, the proposed dose of nitrogen and sulphur seems to be optimal in the soil-plant relationship.

Supplementation of NPK fertilization with sulphur, as demonstrated by our experiment, effectively improves the chemical composition of spring wheat grain. Hence the addition of sulphur to fertilization of spring wheat can be recommended as a means of agronomic biofortification with microelements (Fe, Mn, Zn, and Cu) in areas with low soil sulphur content as well as in conditions of high soil pH. Previous research [4, 26, 104] has shown that the use of sulphur in elemental and sulphate forms promotes higher yield, improves the chemical composition of crops (increases macro- and micronutrient content in triticale and wheat grain and in potato tubes), and increases resistance to fungal and bacterial diseases.

Data Availability

See Table S1 in the Supplementary Material for comprehensive analysis of results from Table 7. All information about the conducted research is available from the corresponding author, e-mail: hanna.klikocka@up.lublin.pl.

Conflicts of Interest

The authors declare that they no conflicts of interest.

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Supplementary Materials

Table S1: comprehensive datasets analysis of Table 7. (*Supplementary Materials*)

References

[1] J. Pieczyńska, A. L. Preschal, R. Weber, J. Biernat, and H. Grajeta, "The effect of cultivation intensity on mineral content in grain, flakes and bran of winter wheat (*Triticum aestivum* L.). Preliminary study," *Roczniki PZH*, vol. 62, no. 2, pp. 199–203, 2011.

[2] H. Klikocka, *"Sulphur Supply in Polish Agriculture", on: "Sulphur Metabolism in Plants"*, A. Sirko, L. J. De Kok, S. Haneklaus et al., Eds., Backhuys Publishers, Leiden, The Netherlands, 2009.

[3] H. Klikocka, "The importance of sulphur in the biosphere and fertilization of plants," *Przemysł Chemiczny*, vol. 90, no. 7, pp. 903–908, 2010, in Polish.

[4] H. Klikocka and M. Cybulska, *Sulphur and Nitrogen Fertilization of Spring Wheat, Mineral Fertilization of Spring Wheat*, Saarbrucken LAP Lambert Academic Publishing, Saarbrücken, Germany, 2014.

[5] H. Klikocka, T. Wyłupek, and B. Narolski, "Sulphur content analysis of Zamość region biosphere," *Ochrona Środowiska*, vol. 37, no. 1, pp. 33–42, 2015.

[6] G. Siebielec, B. Smereczak, A. Klimkowicz-Pawlas et al., *Report from the Third Stage of the Contract Implementation. Monitoring of Chemistry of Arable Soils in Poland in 2015-2017*, IUNG-IB Puławy, Puławy, Poland, 2017, in Polish.

[7] R. D. Graham, R. M. Welch, D. A. Saunders et al., "Nutritious subsistence food system," *Advances in Agronomy*, vol. 92, pp. 1–74, 2007.

[8] WHO 2000, *World Health Report*, World Health Organization, Geneva, Switzerland, 2000.

[9] L. H. Allen, *Ending Hidden Hunger: the History of Micronutrient Deficiency Control, Background Analysis for the World Bank–UNICEF Nutrition Assessment Project*, World Bank, Washington, DC, USA, 2000.

[10] L. A. Allen, B. de Benoist, O. Dary, and R. Hurrell, *Guidelines on Food Fortification with Micronutrients*, World Health Organization and Food and Agricultural Organization of the United Nations, Geneva, Switzerland, 2006.

[11] P. J. White and M. R. Broadley, "Biofortification of crops with seven mineral elements often lacking in human diets-iron, zinc, copper, calcium, magnesium, selenium and iodine," *New Phytologist Journal*, vol. 182, no. 1, pp. 49–84, 2009.

[12] D. D. Miller and R. M. Welch, "Food system strategies for preventing micronutrient malnutrition," *Food Policy*, vol. 42, pp. 115–128, 2013.

[13] R. M. Welch and R. D. Graham, "Breeding crops for enhanced micronutrient content," *Plant and Soil*, vol. 245, no. 1, pp. 205–210, 2002.

[14] P. J. White and M. R. Broadley, "Biofortifing crops with essential mineral elements," *Trends in Plant Science*, vol. 10, no. 12, pp. 586–593, 2005.

[15] M. R. Broadley, P. J. White, R. J. Bryson et al., "Biofortification of UK food crops with selenium," *Proceedings of the Nutrition Society*, vol. 65, no. 2, pp. 169–181, 2006.

[16] B. M. Waters and R. P. Sankaran, "Moving micronutrients from the soil to the seeds: genes and physiological processes from a biofortification perspective," *Plant Science*, vol. 180, no. 4, pp. 562–574, 2011.

[17] Y. Zuo and F. Zhang, "Iron and zinc biofortification strategies in dicots plants by intercropping with gramineous species: a review," *Agronomy for Sustainable Development*, vol. 29, no. 1, pp. 63–71, 2009.

[18] K. Chojnacka, M. Mikulewicz, and J. Cieplik, "Biofortification of food with microelements," *American Journal of Agricultural and Biological Sciences*, vol. 6, no. 4, pp. 544–548, 2011.

[19] R. D. Graham, R. M. Welch, and H. E. Bouis, "Addressing micronutrient malnutrition through enhancing the

nutritional quality of staple foods: principles, perspectives and knowledge gaps," in *Advances in Agronomy*, D. Sparks, Ed., vol. 70, pp. 70–142, Elsevier, New York, NY, USA, 2001.
[20] W. D. Dar, "Macro-benefits from micronutrients for grey to green revolution in agriculture," in *Proceedings of IFA International Symposium on Micronutrients*, New Delhi, India, February 2004.
[21] I. Cakmak, "Plant nutrition research: priorities to meet human needs for food in sustainable ways," *Plant and Soil*, vol. 247, no. 1, pp. 3–24, 2002.
[22] E. Yang, W. R. Chen, and Y. Feng, "Improving human micronutrient through biofortifiction in the soil-plant system: China as a case study," *Environmental Geochemistry and Health*, vol. 29, no. 5, pp. 413–428, 2007.
[23] W. H. Allaway, "Soil-plant-animal and human interrelationships in trace element nutrition," in *Trace Elements in Human and Animal Nutrition*, W. Mertz, Ed., pp. 465–488, Academic Press, Orlando, FL, USA, 1986.
[24] W. A. House and R. M. Welch, "Bioavailability of and interactions between zinc and selenium in rats fed wheat grain intrinsically labeled with 65Zn and 75Se," *Journal of Nutrition*, vol. 119, no. 6, pp. 916–921, 1989.
[25] J. S. Ascher, *Phosphorus and manganese seed coatings for crop growth and yield*, Ph.D. thesis, University of New England, Armidale, Australia, 1994.
[26] H. Klikocka, "The effect of sulphur kind and dose on content and uptake micro-nutrients by potato tubers (*Solanum tuberosum* L.)," *Acta Scientarum Polonarum*, vol. 10, no. 2, pp. 137–151, 2011.
[27] H. Klikocka and A. Głowacka, "Does the sulphur fertilization modify magnesium and calcium content in potato tubers (*Solanum tuberosum* L.)?," *Acta Scientarum Polonorum*, vol. 12, no. 5, pp. 41–53, 2013.
[28] H. Klikocka, B. Barczak, B. Szostak, and A. Kobiałka, "The effect of sulphur and nitrogen fertilization on selenium content and uptake by grain of spring wheat," *Journal of Elementology*, vol. 22, no. 3, pp. 985–994, 2017.
[29] R. C. Jaggi, M. S. Aulakh, and R. Sharma, "Impacts of elemental S applied under various temperature and moisture regimes on pH and available P in acid, neutral alkaline soils," *Biology and Fertility of Soils*, vol. 41, no. 1, pp. 52–58, 2005.
[30] N. W. Scherer, "Sulphur in crop production," *European Journal of Agronomy*, vol. 14, no. 2, pp. 81–111, 2001.
[31] M. M. Safaa, S. M. Khaled, and S. S. Hanan, "Effect of elemental sulphur on solubility of soil nutrients and soil heavy metals and their uptake by maize plants," *Journal of American Science*, vol. 9, no. 12, pp. 19–24, 2013.
[32] A. Głowacka, "The role of intercropping in plant biofortyfication," in *Cropping Systems: Applications, Management and Impact*, J. G. Hodges, Ed., Nova Science Publisher Inc., New York, NY, USA, 2016.
[33] V. H. L. Rodrigo, C. M. Sterling, Z. Teklehaimanot, and A. Nugawela, "Intercropping with banana to improve fractional interception and Radiation-use efficiency of immature rubber plantation," *Field Crops Research*, vol. 69, no. 3, pp. 237–249, 2001.
[34] A. Głowacka, "Uptake of Cu, Zn, Fe and Mn by maize in the strip cropping system," *Plant Soil and Environment*, vol. 59, no. 7, pp. 322–328, 2013.
[35] A. Głowacka, "Changes in the uptake of Cu, Zn, Fe and Mn by dent maize in blue lupine/spring oat strip cropping system," *Zemdirbyste-Agriculture*, vol. 101, no. 1, pp. 41–50, 2014.
[36] H. Klikocka, "Effect of different soil tillage and weed- control methods in potato field experiment on soil physical properties and the content of plant available micro-elements in the soil," *Landbauforschung Völkenrode*, vol. 50, no. 3-4, pp. 133–138, 2000.
[37] H. Klikocka, "Effect of soil tillage and N-fertilization in a spring triticale field experiment on soil physical properties and the content of plant available microelements in the soil," *Landbauforschung Völkenrode*, vol. 50, no. 3-4, pp. 139–144, 2000.
[38] H. Klikocka and C. Sommer, "The effect of different methods of soil tillage and wed control on physical properties in the soil with potato cultivation," *Landbauforschung Völkenrode*, vol. 53, no. 4, pp. 269–277, 2003.
[39] R. M. Welch and R. D. Graham, "A new paradigm for world agriculture: meeting human needs," *Field Crops Research*, vol. 60, no. 1-2, pp. 1–10, 1999.
[40] C. E. Morris and D. C. Sands, "The breeder's dilemma-yield or nutrition?," *National Biotechnology*, vol. 24, no. 9, pp. 1078–1080, 2006.
[41] J. Percival, *The Wheat Plant: A Monograph*, Duckworth, London, UK, 1921.
[42] F. Zhang, M. Fan, X. Gao, Ch. Zou, and Y. Zuo, "Soil and crop management for improving iron and zinc nutrition of crops," in *Development and Uses of Biofortified Agricultural Products*, Taylor & Francis Group, LLC, Oxfordshire UK, 2009.
[43] S. P. McGrath, F. J. Zhao, and S. Fan, "Decreasing mineral concentration in wheat grain over the last 160 years," in *Biogeochemistry of Trace Elements: Environmental Protection Remediation and Human Health*, Y. Zhu, N. Lepp, and R. Naidu, Eds., pp. 281–283, Tsinghua University Press, Beijing, China, 2007.
[44] D. F. Gravin, R. M. Welch, and J. W. Finley, "Historical shifts in the seed mineral micronutrient concentration of US hard red winter wheat germplasm," *Journal of Science Food Agriculture*, vol. 86, no. 13, pp. 2213–2220, 2006.
[45] N. Dickinson, G. Macpherson, A. S. Hursthouse, and J. Atkinson, "Micronutrient deficiencies in maternity and child heath: a review of environmental and social context and implications for Malawi," *Environmental Geochemistry and Health*, vol. 31, no. 2, pp. 253–272, 2009.
[46] http://www.harvestplus.org.
[47] M. Sillanpää, *Micronutrients and the Nutrient Status of Soil: A Global Study*, FAO Soils Bulletin, Rome, Italy, 1982.
[48] M. Nube and R. L. Voortman, *Simultaneously Addressing Micronutrient Deficiencies in Soils, Crops, Animal and Human Nutrition: Opportunities for Higher Yields and Better Health, Staff Working Paper WP-06-02*, Stichting Onderzoek Wereldvoedselvoorziening van de Vrije Universiteit, Centre for World Food Studies, Amsterdam, Netherlands, 2006.
[49] E. Frossard, M. Bucher, F. Mächler, A. Mozafar, and R. Hurrell, "Potential for increasing the content and bioavailability of Fe, Zn and Ca in plants for human nutrition," *Journal of the Science of Food and Agriculture*, vol. 80, no. 7, pp. 861–879, 2000.
[50] A. R. Vicente, G. A. Manganaris, G. O. Sozzi, and C. H. Crisisto, "Nutritional quality of fruies and vegetables," in *Postharvest Handing: A System Approach*, W. J. Florkowski, R. L. Shewfelt, R. Brueckner, and S. E. Prussia, Eds., pp. 81–86, Elsevier INC, New York, NY, USA, 2009.
[51] M. S. Aulakh, "Crop responses to sulphur nutrition," in *Sulphur in Plants*, Y. P. Abrol and A. Ahmed, Eds., pp. 341–358, Kluwer, Boston, MA, USA, 2003.
[52] Z. Rengel, G. D. Batten, and D. E. Crowley, "Agronomic approaches for improving the micronutrient density in

edible portions of field crop," *Field Crops Research*, vol. 60, no. 1-2, pp. 27–40, 1999.

[53] E. B. Erenoglu, U. B. Kutman, Y. Ceylan, B. Yildiz, and I. Cakmak, "Improved nitrogen nutrition enhances root uptake, root-to-shot translocation and remobilization of zinc (65Zn) in wheat," *New Phytologist*, vol. 189, no. 2, pp. 438–448, 2011.

[54] Y. F. Xue, S. C. Yue, Y. Q. Zhang et al., "Grain and shoot zinc accumulation in winter wheat affected by nitrogen management," *Plant and Soil*, vol. 361, no. 1-2, pp. 153–163, 2012.

[55] U. B. Kutman, B. Y. Kutman, T. Ceylan, E. A. Ova, and I. Cakmak, "Contributions of root uptake and remobilization to grain zinc accumulation in wheat depending on post-anthesis zinc availability and nitrogen nutrition," *Plant and Soil*, vol. 361, no. 1-2, pp. 177–187, 2012.

[56] R. Shi, Y. Zhang, X. Chen et al., "Influence of long-term nitrogen fertilization on micronutrient density in grain of winter wheat (*Triticum aestivum* L.)," *Journal of Cereal Science*, vol. 51, no. 1, pp. 165–170, 2010.

[57] C. Q. Zou, Y. Q. Zhang, A. Rashid et al., "Biofortification of wheat with zinc through zinc fertilization in seven countries," *Plant and Soil*, vol. 361, no. 1-2, pp. 119–130, 2012.

[58] Y. M. Wang and P. B. F. Outworker, "Molecular and environmental factors determining grain quality in rice," *Food and Energy Security*, vol. 1, no. 2, pp. 111–132, 2012.

[59] L. H. Rodriguez, D. A. Morales, E. R. Rodriguez, and C. D. Romero, "Minerals and trace elements in a collection of wheat landraces from the Canary Islands," *Journal of Food Compositions and Analysis*, vol. 24, no. 8, pp. 1081–1090, 2011.

[60] http://www.fao.org.statistics/en.

[61] H. Branch-Pedersen, S. Borg, B. Taurus, and P. B. Holm, "Molecular genetics approaches to increasing mineral availability of vitamin content of cereals," *Journal of Cereal Science*, vol. 46, no. 3, pp. 308–326, 2007.

[62] Z. Lončarić, B. Popović, K. Karalić, Z. Jurković, A. Nevistić, and M. Engler, "Soil chemical properties and wheat genotype impact on micronutrient and toxic elements content in wheat integral flour," *Medicinski Glasnik*, vol. 9, pp. 97–103, 2012.

[63] Y. Xu, A. An, H. Li, and H. Xu, "Review: breeding what for enhanced micronutrients," *Canadian Journal of Plant Science*, vol. 91, no. 2, pp. 231–237, 2011.

[64] T. Teklić, Z. Lončarić, V. Kovačević, and B. R. Singh, "Metallic trace elements in cereal grain–a review: how much metal do we eat?," *Food and Energy Security*, vol. 2, no. 2, pp. 81–95, 2013.

[65] E. Schnug and H. Beringer, *Sulphur in Agroecosystems*, Kluwer Academic Publishers, Dordrecht, Netherlands, 1998.

[66] S. Haneklaus, E. Bloem, and E. Schnug, "The global cycle and its links to plant environment," in *Sulphur in Plants*, Y. P. Abrol and A. Ahmad, Eds., pp. 1–28, Kluwer Publishers, Dordrecht, Netherlands, 2003.

[67] J. Balik, M. Kulhanek, J. Černy et al., "Differences in soil sulfur fractions due to limitation of atmospheric deposition," *Plant, Soil Environment*, vol. 55, no. 8, pp. 344–352, 2009.

[68] H. Klikocka, M. Cybulska, and A. Nowak, "Efficiency of fertilization and utilization of nitrogen and sulphur by the spring wheat," *Polish Journal of Environmental Studies*, vol. 26, no. 5, pp. 2029–2036, 2017.

[69] A. Podleśna, J. Podleśny, and H. Klikocka, "Effect of fertilization with sulphur and nitrogen-phosphorus management of maize," *Przemysł Chemiczny*, vol. 96, no. 6, pp. 1374–1377, 2017, in Polish.

[70] H. Klikocka, S. Haneklaus, E. Bloem, and E. Schnug, "Influence of sulphur fertilization on infection of potato tubers with *Rhizoctonia solani* and *Streptomyces scabies*," *Journal of Plant Nutrition*, vol. 28, no. 5, pp. 819–833, 2005.

[71] W. Grzebisz and R. Häedter, *Kieserite–Natural Magnesium Sulphate*, Verlagsgesseischaft für Ackerbau GmbH, Kassel, Germany, 2006, in Polish.

[72] H. Hesse, V. Nikiforova, B. Gakiere, and R. Hoefgen, "Molecular analysis and control of cysteine biosynthesis: integration of nitrogen and sulphur metabolism," *Journal of Expermimental Botany*, vol. 55, no. 401, pp. 1283–1292, 2004.

[73] A. Podleśna, "Studies on role of sulfur at forming of mineral management and height and quality of chosen crops yield," Habilitation thesis, Monografie i Rozprawy Naukowe, no. 37, IUNG Puławy, Puławy, Poland, 2013, in Polish.

[74] W. Grzebisz, "Technologies fertilization of crops," in *Grain and Corn*, vol. 2, p. 279, PWRiL, Poznań, Poland, 2012, in Polish.

[75] C. A. Pedersen, L. Knudsen, and E. Schnug, "Sulphur fertilization," in *Sulphur in Agroecosystems*, E. Schnug and H. Beringer, Eds., pp. 115–134, Kluwer Academic Publ., Dordrecht, Netherlands, 1998.

[76] B. Filipek-Mazur, A. Lepiarczyk, and K. Gondek, "Effect of sulphur fertilizer on yields and composition of wheat grains elementary. Part II. The contents of the macro-elements," *Zeszyty Problemowe Postępów Nauk Rolniczych*, vol. 556, pp. 79–84, 2010, in Polish.

[77] W. Grzebisz, *Fertilization of Crops. Part I. Basics of Fertilizing*, PWRiL, Poznań, Poland, in Polish.

[78] A. Ciołek, E. Makarska, M. Wesołowski, and R. Cierpiała, "Content of selected nutrients in wheat, barley and oat from organic and conventional farming," *Journal of Elementology*, vol. 17, no. 2, pp. 181–189, 2012.

[79] J. Korzeniowska, E. Stanisławska-Glubiak, K. Kantek, W. Lipiński, and R. Gaj, "Micronutrient status of winter wheat in Poland," *Journal of Central European Agriculture*, vol. 16, no. 1, pp. 54–64, 2015.

[80] X. Gao, O. M. Lukow, and C. A. Grant, "Grain concentrations of protein, Fe and Zn and bread making quality in spring wheat as affected by seeding date and nitrogen fertilizer management," *Journal of Geochemical Exploration*, vol. 121, pp. 36–44, 2012.

[81] A. Woźniak and A. Stępniowska, "Yield and quality of durum wheat grain in different tillage systems," *Journal of Elementology*, vol. 22, no. 3, pp. 817–829, 2017.

[82] K. Wojtkowiak, A. Stępień, R. Pitrzak-Fiećko, and M. Warechowska, "Effects of nitrogen fertilization on the yield, micronutrient content and fatty acid profiles of winter wheat (*Triticum aestivum* L.) varieties," *Journal of Elementology*, vol. 23, no. 2, pp. 483–494, 2018.

[83] D. J. Pilbeam, "Nitrogen," in *Handbook of Plant Nutrition*, A. V. Barker and D. J. Pilbeam, Eds., pp. 17–63, CRC PressTaylor & Francis Group, New York, NY, USA, 2nd edition, 2015.

[84] U. B. Kutman, B. Yildiz, and I. Cakmak, "Improved nitrogen status enhances Zn and Fe concentrations both in the whole grain and the endosperm fraction of wheat," *Journal of Cereal Science*, vol. 53, no. 1, pp. 118–125, 2011.

[85] D. E. Williams and J. Vlamis, "Comparative accumulation of manganese and boron in barley tissues," *Plant and Soil*, vol. 33, no. 1–3, pp. 623–628, 1971.

[86] L. M. Shuman, "Micronutrient fertilizers," *Journal of Crop Production*, vol. 1, no. 2, pp. 165–195, 1998.

[87] M. F. Soliman, S. F. Kostandii, and M. L. van Beusichem, "Influence of sulphur and nitrogen fertilizer on the uptake of

iron, manganese, and zinc by corn plants grown in calcareous soil," *Communication of Soil Science and Plant Analysis*, vol. 23, no. 11-12, pp. 1289–1300, 1992.

[88] F. J. Zhao, Y. H. Su, S. J. Dunham et al., "Variation in mineral micronutrient concentrations in grain of wheat lines of diverse origin," *Journal of Cereal Science*, vol. 49, no. 2, pp. 290–295, 2009.

[89] V. D. Fageria, "Nutrient interactions in crop plants," *Journal of Plant Nutrition*, vol. 24, no. 8, pp. 1269–1290, 2001.

[90] A. J. Hiatt and J. E. Leggett, "Ionic interactions and antagonisms in plant," in *The Plant Root and Its Environment*, E. W. Carson, Ed., pp. 101–143, University Press of Virginia, Charlottesville, VA, USA, 1974.

[91] W. Grzebisz, *Fertilization of Crops. Part II. Fertilizers and Fertilization Systems. The Basis of Fertilizing*, PWRiL Poznań, Poznań, Poland, 2009, in Polish.

[92] O. Oenema and R. Postma, "Managing sulphur in agroecosystems," in *Sulphur in Plants*, Y. P. Abrol and A. Ahmad, Eds., pp. 45–70, Kluwer Academic Publ., Dordrecht, Netherlands, 2003.

[93] P. J. Randall, K. Spencer, and J. R. Freney, "Sulphur and nitrogen fertilizer effects on wheat. I. Concentrations of sulphur and nitrogen and the nitrogen to sulphur ration in grain, in relation to the yield response," *Australian Journal of Agricultural Research*, vol. 32, no. 2, pp. 203–212, 1981.

[94] A. Inal, A. Günes, M. Alphaslan et al., "Diagnosis of sulphur deficiency and effects of sulphur on yield and yield components of wheat grown in central Anatolia," *Turkey Journal of Plant Nutrition*, vol. 26, no. 7, pp. 1483–1498, 2003.

[95] M. O. Johnson, "Manganese as a cause of the depression of the assimilation by iron by pineapple plants," *Industrial & Engineering Chemistry*, vol. 9, no. 1, pp. 47–49, 1917.

[96] H. Maschner, *Mineral Nutrition of Higher Plants*, Academic Press, Boston, MA, USA, 2nd edition, 1995.

[97] A. M. Michaud, C. Chappellaz, and P. Hinsiger, "Copper phytotoxicity affects root elongation and iron nutrition in durum wheat (*Triticum turgidum durum* L.)," *Plant and Soil*, vol. 310, no. 1-2, pp. 151–165, 2008.

[98] L. V. Kochian, "Mechanism of micronutrient uptake and translocation in plants," in *Micronutrients in Agriculture*, J. J. Mortvedt, F. R. Cox, L. M. Shuman, and R. M. Welch, Eds., pp. 29–296, Soil Science Society of America, Madison, WI, USA, 1991.

[99] L. A. del Rio, F. Sevilla, M. Gómez, J. Yàńez, and J. López-Gorgé, "Superoxide dismutase: an enzyme system for the study of micronutrient interactions in plants," *Planta*, vol. 140, no. 3, pp. 221–225, 1978.

[100] Z. Rengel and R. D. Graham, "Wheat genotypes differ in Zn efficiency when grown in chelate-buffered nutrient solution. II. Nutrient uptake," *Plant and Soil*, vol. 176, no. 2, pp. 317–324, 1995.

[101] Z. Dmowski, H. Dzieżyc, and L. Nowak, "The assessment of the impact of selected parameters, precipitation, and soil for yielding of spring wheat in the South-Westen Polish," *Acta Agrophysica*, vol. 11, no. 3, pp. 613–622, 2008, in Polish.

[102] E. Radzka, G. Koc, and A. Bombik, "The influence of the drought on the yielding of spring wheat in eastern Poland," *Acta Agrophysica*, vol. 13, no. 2, pp. 445–454, 2009, in Polish.

[103] Z. Dmowski and H. Dzieżyc, "The Reed for runoff of spring wheat on soils of good wheat and rye very good in North-Eastern Poland," *Acta Agrophysica*, vol. 13, no. 1, pp. 39–48, 2009, in Polish.

[104] H. Klikocka, "The influence of enriched NPK fertilization with S, Mg and contained of micronutrients liquid fertilizer Insol 7 on potato tubers yield (*Solanum tubersoum* L.) and infestation of tubers with *Streptomyces scabies* and *Rhizoctonia solani*," *Journal of Elementology*, vol. 14, no. 2, pp. 271–288, 2009.